SUPPORTING INFORMATION

Synthesis of Highly Cis, Syndiotactic ROMP Polymers Using Ruthenium Metathesis Catalysts

Lauren E. Rosebrugh, Vanessa M. Marx, Benjamin K. Keitz, Robert H. Grubbs*

Arnold and Mabel Beckman Laboratory of Chemical Synthesis, Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125, United States

Table of Contents

List of Figures

General Information.

All reactions were carried out in dry glassware under an argon atmosphere using standard Schlenk techniques or in a Vacuum Atmospheres Glovebox under a nitrogen atmosphere, unless otherwise specified. All solvents were purified by passage through solvent purification columns and further degassed by bubbling argon. C_6D_6 was purified by passage through a solvent purification column. $CDCl_3$, CD_2Cl_2 and THF-d_8 were used as received. Monomers **6**[1] and **7**[2] were synthesized according to the literature procedures, while monomer **5** was purchased from Sigma Aldrich and used as received. $RuCl_2(PCy_3)(=CH\text{-}o\text{-}O^iPrC_6H_4)$ (**S3**) was obtained from Materia, Inc. 2-Bromo-*N*-(2-*iso*-propyl-6-methylphenyl)acetamide (**S5**)[3] and 1-*tert*-butyl-3-mesityl-4,5-dihydro-1*H*-imidazol-3-ium (**S2**)[4] were synthesized according to literature procedures. Silica gel was dried under vacuum at 200 °C for 48 h prior to use in the glovebox. Other commercially available reagents were used as received.

^1H NMR spectra were acquired at 500 MHz and ^{13}C NMR spectra at 126 MHz as $CDCl_3$ or C_6D_6 solutions unless otherwise noted. Chemical shifts are reported in ppm downfield from Me_4Si by using the residual solvent peak as an internal standard. Spectra were analyzed and processed using MestReNova Ver. 7.1.

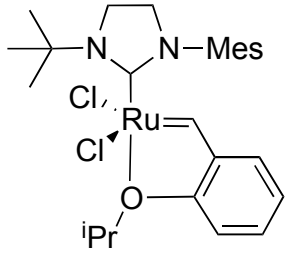
High-resolution mass spectra (HRMS) were provided by the California Institute of Technology Mass Spectrometry Facility using a JEOL JMS-600H High Resolution Mass Spectrometer. All HRMS were by FAB+ ionization, except where specified.

Polymer molecular weights were determined by multi-angle light scattering (MALS) gel permeation chromatography (GPC) using a miniDAWN TREOS light scattering detector, a Viscostar viscometer, and an OptilabRex refractive index detector, all from Wyatt Technology. An Agilent 1200 UV-Vis detector was also

---

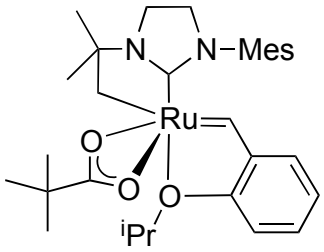
[1] Tabor, D.C.; White, F.H.; Collier, L.W.; Evans, S.A. *J. Org. Chem.* **1983**, *48*, 1638.
[2] (a) O'Dell, R.; McConville, D. H.; Hofmeister, G. E.; Schrock, R. R. *J. Am. Chem. Soc.* **1994**, *116*, 3414. (b) Maier, G.; Jung, W. A. Chem. Ber. **1982**, *125*, 804.
[3] Rosebrugh, L. M.; Herbert, M. B.; Marx, V. M.; Keitz, B. K.; Grubbs, R. H. *J. Am. Chem. Soc.* **2013**, *135*, 1276.
[4] Ledoux, N.; Allaert, B.; Pattyn, S.; Vander Mierde, H.; Vercaemst, C.; Verpoort, F. *Chem. Eur. J.* **2006**, *12*, 4654.

present in the detector stack. Absolute molecular weights were determined using dn/dc values calculated by assuming 100% mass recovery of the polymer sample injected into the GPC. No internal standards were used. Differential Scanning Calorimetry (DSC) was performed using a Perkin Elmer DSC 7 at a nitrogen flow rate of 40 mL/min and a heating rate of 2 K/min^{-1} from 0 °C to 200 °C. Thermogravimetric analysis (TGA) was performed using a TA Instruments O5000 TGA at a nitrogen flow rate of 10 mL/min (sample) and 25 mL/min (balance).



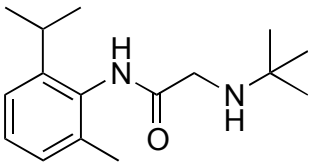
Preparation of S1.

In a glovebox, a solution of **S2** (0.19 g, 0.66 mmol) in hexanes (20 mL) was treated with $KCOMe_2Et$ (88 mg, 0.69 mmol), and the mixture was allowed to stir at room temperature for 2 h. To the reaction mixture was then added **S3** (0.38 g, 0.64 mmol), upon which the mixture was removed from the glove box and allowed to stir at 65 °C overnight (12 h). The precipitated solids were filtered and washed well with warm hexanes and pentane, and then collected with CH_2Cl_2 and concentrated. The crude mixture was further purified by flash column chromatography (SiO_2, eluent pentane to 20% Et_2O in pentane to CH_2Cl_2) to provide **S1** as a green powder. ^1H NMR (500 MHz, $CDCl_3$) δ 16.87 (s, 1H), 7.56 (m, 1H), 7.07 (s, 2H), 6.97–6.89 (m, 3H), 6.87 (m, 1H), 5.08 (hept, *J* = 6.2 Hz, 1H), 4.10–3.82 (m, 4H), 2.46 (s, 3H), 2.26–2.27 (m, 15H), 1.62 (d, *J* = 6.2 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 312.9, 207.5, 152.6, 145.7, 139.4, 138.6, 138.2, 130.9, 129.7, 124.0, 122.8, 113.3, 74.5, 56.3, 51.6, 46.1, 29.8, 22.5, 21.3, 18.4. HRMS (FAB+): Calculated—564.1249, Found—564.1268.



Preparation of 2.

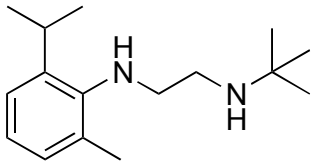
In a glovebox, a 20 mL scintillation vial was charged with **S1** (0.11 g, 0.20 mmol), NaOPiv (0.25 g, 2.0 mmol), THF (4.0 mL), and MeOH (2.0 mL). The vial was capped, removed from the glovebox, and heated to 40 °C for 5 h at which point a color change from green to brown to dark purple was observed. The vial was returned to the box, where the solvent was removed under high vacuum and the residue dissolved in CH_2Cl_2 (30 mL), filtered through celite, and concentrated to a deep purple residue. The crude mixture was purified by pipette column (SiO_2, eluent 20% Et_2O in pentane) three times and subsequently recrystallized from pentane to provide **2** as a bright purple solid (59 mg, 22%). ^{1}H NMR (500 MHz, THF-d_8) δ 14.69 (s, 1H), 7.44–7.36 (m, 1H), 7.32 (m, 1H), 7.07 (m, 1H), 6.88 (m, 1H), 6.72 (s, 2H), 5.04 (hept, *J* = 6.2 Hz, 1H), 3.95–3.72 (m, 4H), 2.82 (d, *J* = 10 Hz, 1H), 2.38 (s, 3H), 2.38 (*overlapped*, 1H), 2.14 (s, 3H), 2.13 (s, 3H), 1.45 (d, *J* = 6.2 Hz, 3H), 1.44 (s, 3H), 1.38 (d, *J* = 6.2 Hz, 3H), 0.87 (s, 9H), 0.57 (s, 3H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 260.3, 211.4, 188.2, 155.0, 143.7, 137.9, 137.6, 137.0, 136.8, 129.9, 129.2, 126.2, 123.4, 122.7, 114.1, 75.8, 62.6, 51.1, 47.7, 43.9, 39.6, 29.4, 28.1, 23.2, 22.2, 22.0, 21.1, 18.8, 18.7. HRMS (FAB+, (M+H)-H_2): Calculated—593.2318, Found—593.2327.



Preparation of 2-(*tert*-butylamino)-*N*-(2-isopropyl-6-methylphenyl)acetamide (S4).

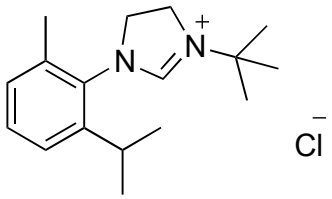
S5 (7.2 g, 27 mmol) and *tert*-butylamine (4.2 mL, 39 mmol) were dissolved in MeCN (90 mL), K_2CO_3 (5.7 g, 42 mmol) was added, and the solution was refluxed for

24 h. After cooling to room temperature, the mixture was filtered over celite and concentrated. The residue was then dissolved in CH_2Cl_2 and filtered over a pad of silica gel (eluent 10% MeOH in CH_2Cl_2). Removal of the solvent *in vacuo* provided **S4** (6.7 g, 94%) as an off-white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.09 (br s, 1H), 7.18 (m, 1H), 7.16 (m, 1H), 7.09 (m, 1H), 3.41 (s, 2H), 3.03 (m, 1H), 2.22 (s, 3H), 1.71 (br s, 1H), 1.20 (d, *J* = 6.9 Hz, 6H), 1.17 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.6, 145.2, 135.6, 132.8, 128.2, 127.5, 123.4, 51.3, 46.1, 29.1, 28.7, 23.4, 18.8. HRMS (FAB+, (M+H)): Calculated—263.2123, Found—263.2111.



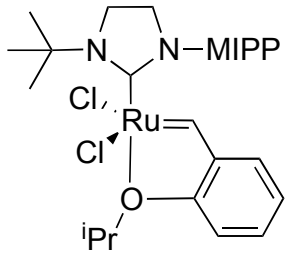
Preparation of *N1*-(tert-butyl)-*N2*-(2-isopropyl-6-methylphenyl)ethane-1,2-diamine (S6).

A solution of compound **S4** (6.7 g, 26 mmol) in THF (10 mL) was added to a 0 °C solution of lithium aluminum hydride (3.0 g, 79 mmol) in THF (100 mL), and the solution was brought to room temperature, then refluxed for 72 h. The mixture was then cooled to 0 °C, and water (3 mL), 10% *aq.* NaOH (3 mL), then additional water (3 mL) were added sequentially. The solution was dried with $MgSO_4$, filtered, and concentrated. Flash chromatography of the residue (SiO_2, using 10% MeOH in CH_2Cl_2) provided **S6** (3.7 g, 57%) as a pale yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.09 (m, 1H), 6.98 (m, 1H), 6.91 (m, 1H), 3.29 (m, 1H), 3.00 (m, 2H), 2.80 (m, 2H), 2.33 (s, 3H), 1.24 (d, *J* = 6.9 Hz, 6H), 1.13 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.2, 140.7, 130.5, 128.4, 123.6, 122.4, 50.6, 50.3, 42.8, 29.2, 27.5, 24.0, 19.0. HRMS (FAB+, (M+H)): Calculated—249.2331, Found—249.2335.



Preparation of 3-(*tert*-Butyl)-1-(2-isopropyl-6-methylphenyl)-4,5-dihydro-1H-imidazol-3-ium chloride (S7).

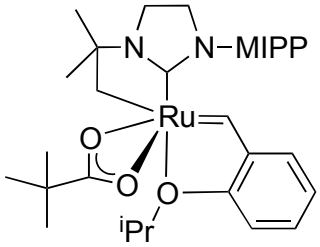
A solution of compound **S6** (3.5 g, 14 mmol) in Et_2O (25 mL) was treated with HCl (14 mL, 2 M in Et_2O), and stirred for 15 minutes at room temperature. The solid was then filtered, washed with Et_2O, dried, suspended in $CH(OEt)_3$ (25 mL), and refluxed for 2 h. The solution was cooled to room temperature, and then concentrated. The resulting solid residue was washed rigorously with Et_2O to provide **S7** (1.5 g, 37%) as an off-white solid. ^1H NMR (500 MHz, $CDCl_3$) δ 9.02 (br s, 1H), 7.31 (m, 1H), 7.22 (m, 1H), 7.12 (m, 1H), 4.49 (m, 1H), 4.38 (m, 2H), 4.22 (m, 1H), 2.91 (m, 1H), 2.40 (s, 3H), 1.61 (s, 9H), 1.27 (m, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.0, 146.4, 135.9, 132.0, 130.5, 129.2, 124.8, 57.8, 52.4, 46.5, 28.6, 28.4, 24.8, 24.2, 18.6. HRMS (FAB+, (M-Cl)): Calculated—259.2174, Found—259.2172.



Preparation of S8.

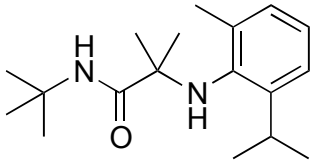
In a glovebox, $KCOMe_2Et$ (0.15 g, 1.2 mmol) was added to a suspension of compound **S7** (0.29 g, 1.0 mmol) in hexanes (12 mL). The solution was stirred at 35 °C for 30 minutes, and then **S3** (0.60 g, 1.0 mmol) was added, and then removed from the glovebox. The solution was stirred for 3 h at 65 °C and subsequently cooled to room temperature. The resulting precipitate was filtered, washed with warm hexanes, and further purified by column chromatography (SiO_2, eluent pentane to 20% Et_2O in pentane to DCM) to provide **S8** (0.55 g, 92%) as a green solid. ^1H NMR (500 MHz, $CDCl_3$) δ 16.86 (s, 1H), 7.54 (m, 1H), 7.49 (m, 1H), 7.41 (m, 1H), 7.23 (m,

1H), 6.94 (m, 1H), 6.88 (m, 1H), 6.85 (m, 1H), 5.07 (hept, *J* = 6.2 Hz, 1H), 4.02 (m, 2H), 3.91 (m, 2H), 3.17 (hept, *J* = 6.8 Hz, 1H), 2.33 (s, 3H), 2.28 (s, 9H), 1.67 (d, *J* = 6.2 Hz), 1.59 (d, *J* = 6.2 Hz, 3H), 1.19 (d, *J* = 6.8 Hz, 3H), 0.89 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 311.0, 207.8, 152.7, 148.8, 145.0, 140.4, 138.0, 130.7, 129.1, 129.0, 124.8, 123.9, 122.6, 113.2, 74.5, 56.3, 53.1, 46.0, 29.8, 27.6, 25.6, 23.8, 22.7, 22.3, 19.0. HRMS (FAB+, (M)): Calculated—578.1405, Found—578.1433.



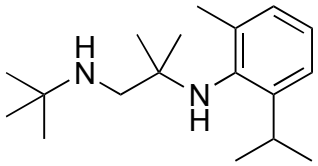
Preparation of 3.

In a glovebox, a solution of sodium pivalate (0.22 g, 1.7 mmol) in MeOH (3 mL) was added to a solution of compound **S8** (0.10 g, 0.17 mmol) in THF (6 mL). The mixture was removed from the glovebox, heated at 50 °C for 12 h, and then brought back into the glovebox and concentrated. The residue was dissolved in CH_2Cl_2, filtered over a pad of celite, and concentrated. The crude mixture was subjected to purification over a plug of silica gel (eluent pentanes to 20% Et_2O in pentanes), then recrystallized from hexanes to provide **6** (65 mg, 65%) as a bright purple solid. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 14.70 (s, 1H), 7.45 (m, 1H), 7.39 (m, 1H), 7.08 (m, 1H), 7.07 (m, 1H), 7.02 (m, 1H), 6.94 (m, 1H), 4.99 (hept, *J* = 6.4 Hz), 3.92–3.79 (m, 3H), 3.79–3.69 (m, 2H), 2.79 (d, *J* = 6.8 Hz, 1H), 2.45 (d, *J* = 6.8 Hz, 1H), 2.17 (s, 3H), 1.47 (s, 3H), 1.44 (d, *J* = 6.4 Hz), 1.40 (d, *J* = 6.4 Hz, 3H), 1.24 (d, *J* = 6.9 Hz, 3H), 1.10 (d, *J* = 6.9 Hz, 3H), 0.91 (s, 9H), 0.56 (s, 3H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 260.2, 210.9, 187.5, 154.5, 147.5, 143.2, 138.4, 137.5, 128.3, 127.5, 125.6, 123.8, 122.9, 122.3, 113.8, 75.5, 62.1, 51.8, 47.3, 43.4, 39.1, 28.8, 27.9, 27.7, 25.5, 23.7, 22.8, 21.8, 21.7, 18.7. HRMS (FAB+, (M)): Calculated—608.2552, Found—608.2536.



Preparation of *N*-(*tert*-Butyl)-2-((2-isopropyl-6-methylphenyl)amino)-2-methylpropanamide (S9).

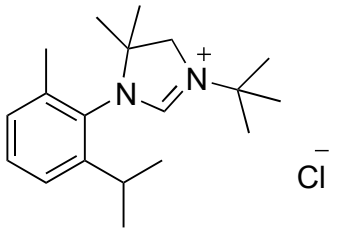
2-Bromo-2-methylpropionyl bromide (4.1 g, 33 mmol) was dissolved in CH_2Cl_2 (60 mL), *tert*-butylamine (3.2 mL, 30 mmol) followed by Et_3N (12 mL, 60 mmol) were added dropwise, and the mixture was stirred overnight at room temperature. The solution was washed with saturated NH_4Cl (*aq.*) (x2), dried with Na_2SO_4, and concentrated. The residue was then dissolved in THF (75 mL), cannulated into a solution of 2-isopropyl-6-methylaniline (5.0 g, 33 mmol) and NaH (1.4 g, 60 mmol) in THF (75 mL), and stirred overnight at room temperature. The solution was diluted with EtOAc, washed with saturated NH_4Cl (*aq.*), brine, and dried with Na_2SO_4, and concentrated. Purification by column chromatography (SiO_2, eluent 10% MeOH in CH_2Cl_2) and removal of the solvent *in vacuo* provided **S9** (2.9 g, 33%) as a peach solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (br s, 1H), 7.10 (m, 1H), 6.98 (m, 2H), 3.17 (br s, 1H), 3.11 (m, 1H), 2.27 (s, 3H), 1.40 (s, 9H), 1.30 (s, 6H), 1.20 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 176.9, 143.4, 141.3, 132.7, 128.5, 124.1, 123.7, 60.3, 50.2, 28.5, 28.2, 27.1, 23.7, 20.7. HRMS (EI+, (M+H)): Calculated—291.2436, Found—291.2429.



Preparation of *N1*-(*tert*-Butyl)-*N2*-(2-isopropyl-6-methylphenyl)-2-methylpropane-1,2-diamine (S10).

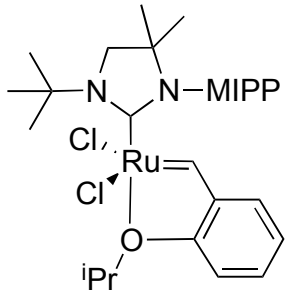
A solution of BH_3·THF (43 mL, 1 M in THF), was added dropwise to a 0 °C solution of compound **S9** (2.5 g, 8.6 mmol) in THF (12 mL). The mixture was stirred overnight at room temperature, and then quenched via dropwise addition of MeOH at 0 °C and concentrated. The residue was then re-dissolved in MeOH and re-

concentrated (x3). Purification by column chromatography (SiO_2, eluent CH_2Cl_2 then 10% MeOH in CH_2Cl_2) and removal of the solvent *in vacuo* provided **S10** (1.2 g, 50%) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.09 (m, 1H), 7.00 (m, 1H), 6.97 (m, 1H), 3.53 (m, 1H), 2.60 (2, 2H), 2.37 (s, 3H), 1.18 (d, *J* = 6.9 Hz, 6H), 1.15 (s, 9H), 1.06 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.5, 142.6, 135.2, 128.1, 123.4, 123.2, 56.0, 54.9, 49.9, 29.3, 27.5, 26.7, 24.1, 20.8. HRMS (EI+, (M+H)): Calculated—277.2644, Found—277.2636.



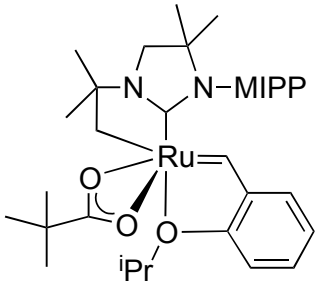
Preparation of 3-(*tert*-Butyl)-1-(2-isopropyl-6-methylphenyl)-5,5-dimethyl-4,5-dihydro-1H-imidazol-3-ium chloride (S11).

A solution of compound **S10** (1.1 g, 4.0 mmol) in Et_2O (10 mL) was treated with HCl (4.0 mL, 2 M in Et_2O), and stirred for 15 minutes at room temperature. The solid was then filtered, washed with Et_2O, dried, suspended in $CH(OEt)_3$ (10 mL), and refluxed for 2 h. The solution was cooled to room temperature, and then concentrated. The resulting solid residue was washed rigorously with Et_2O to provide **S11** (0.6 g, 46%) as a colorless solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.26 (br s, 1H), 7.30 (m, 1H), 7.21 (m, 1H), 7.13 (m, 1H), 4.07 (d, *J* = 12 Hz, 1H), 4.02 (d, *J* = 12 Hz, 1H), 2.85 (m, 1H), 2.41 (s, 3H), 1.60 (s, 9H), 1.48 (s, 3H), 1.41 (s, 3H), 1.29 (d, *J* = 6.8 Hz, 3H), 1.16 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.7, 148.3, 137.8, 130.3, 129.7, 128.9, 124.7, 69.7, 58.7, 57.8, 29.2, 28.3, 26.9, 26.4, 25.9, 22.7, 20.5. HRMS (FAB+, (M-Cl)): Calculated—287.2487, Found—287.2499.



Preparation of S12.

In a glovebox, $KCOMe_2Et$ (57 mg, 0.45 mmol) was added to a suspension of compound **S11** (0.14 g, 0.43 mmol) in hexanes (13 mL). The solution was stirred at room temperature for 2 h, and then **S3** (0.31 g, 0.52 mmol) was added, at which point the solution was removed from the glovebox. The solution was stirred for 3 h at 65 °C and then cooled to room temperature. The resulting precipitate was filtered, washed thoroughly with warm hexanes, and further purified by column chromatography (SiO_2, eluent pentane to 20% Et_2O in pentane to CH_2Cl_2) to provide **S12** (0.21 g, 86%) as a green solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 16.66 (s, 1H), 7.57–7.42 (m, 3H), 7.24–7.20 (m, 1H), 6.93 (d, *J* = 8.4 Hz, 1H), 6.90–6.83 (m, 2H), 5.06 (hept, *J* = 6.3 Hz, 1H), 3.84 (d, *J* = 9.9 Hz, 1H), 3.65 (d, *J* = 9.8 Hz, 1H), 3.25 (hept, *J* = 6.7 Hz, 1H), 2.29 (*overlapped*, 12H), 1.68 (d, *J* = 6.2 Hz, 3H), 1.58 (d, *J* = 6.2 Hz, 3H), 1.40 (s, 3H), 1.24 (d, *J* = 6.8 Hz, 3H), 1.12 (s, 3H), 0.75 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 310.79, 207.99, 152.78, 150.31, 144.75, 140.38, 138.56, 130.61, 129.54, 128.67, 125.33, 124.12, 122.65, 113.34, 74.45, 65.40, 61.19, 56.32, 29.79, 28.33, 27.99, 25.63, 25.26, 23.92, 22.86, 22.29, 21.32. HRMS (FAB+, $(M+H)-H_2$): Calculated—605.1640, Found—605.1618.



Preparation of 4.

In a glovebox, a 20 ml scintillation vial was charged with **S12** (60 mg, 0.10 mmol), NaOPiv (0.12 g, 1.0 mmol), THF (2.0 mL), and MeOH (2.0 mL). The vial was capped, removed from the glovebox, and heated to 40 °C for 21 h at which point a color change from green to brown to dark purple was observed. The vial was returned to the box, where the solvent was removed under high vacuum and the residue dissolved in CH_2Cl_2 (15 mL), filtered through celite, and concentrated to a deep purple residue. The residue was purified by pipet column (SiO_2, eluent 20% Et_2O in pentane) and subsequently recrystallized from hexanes to provide **8** as a bright purple solid (25 mg, 40%). ^{1}H NMR (500 MHz, C_6D_6) δ 14.98 (s, 1H), 7.47 (dd, *J* = 7.4, 1.7 Hz, 1H), 7.23 (td, *J* = 8.0, 1.7 Hz, 1H), 7.07 (*overlapped*, 2H), 6.97–6.99 (m, 1H), 6.88 (t, *J* = 7.4 Hz, 1H), 6.60 (d, *J* = 8.3 Hz, 1H), 4.63 (hept, *J* = 6.3 Hz, 1H), 3.98 (hept, *J* = 6.8 Hz, 1H), 3.35–3.21 (m, 2H), 2.80–2.69 (m, 2H), 2.32 (s, 3H), 1.46 (d, *J* = 6.4 Hz, 3H), 1.40 (s, 3H), 1.35 (s, 3H), 1.31 (d, *J* = 6.9 Hz, 3H), 1.24 (d, *J* = 6.1 Hz, 3H), 1.18 (s, 9H), 1.12 (d, *J* = 6.9 Hz, 3H), 0.76 (s, 3H), 0.61 (d, *J* = 9.0 Hz, 3H). ^{13}C NMR (126 MHz, C_6D_6) δ 260.95, 211.46, 187.86, 155.35, 149.68, 144.03, 139.68, 136.90, 128.69, 127.87, 127.57, 125.73, 124.69, 123.15, 122.70, 113.79, 75.07, 64.80, 62.12, 57.77, 47.76, 39.61, 30.87, 28.77, 28.69, 28.39, 25.63, 24.67, 24.12, 22.87, 22.01, 21.82, 20.68. HRMS (FAB+, (M+H)-H_2): Calculated—635.2787, Found—635.2788.

General Procedure for the Determination of Initiation Rates.

In a glovebox, a 4 mL vial was charged with catalyst (0.012 mmol) and diluted with 1 mL C_6D_6 to create a stock solution (0.012 M). A portion of the stock solution (0.25 mL, 0.003 mmol catalyst) was added to an NMR tube and diluted with C_6D_6 (0.35 mL). The NMR tube was sealed with a septa cap and placed in the NMR

spectrometer at 30 °C. Butyl vinyl ether (12 μL, 0.09 mmol) was added and the disappearance of the benzylidene proton resonance was monitored by arraying the 'pad' function in VNMRj.

All reactions showed clean first-order kinetics over a period of at least three half-lives. Spectra were baseline corrected and integrated with MestReNova. Estimation of error was determined from the average of three different kinetic runs.

General Polymerization Procedure.

In a glovebox, a solution of catalyst was prepared from **2** (24 mg, 40 μmol) and THF (6 mL) and added to a Schlenk flask. On a vacuum manifold, a separate Schlenk flask was flame-dried and charged with monomer (4.0 mmol) and THF (10 mL) to make a stock solution. The monomer solution was degassed via freeze-pump-thaw (3X). An aliquot (2.5 mL, 1.0 mmol) of monomer stock solution was added via gas-tight syringe to an air-tight vial with a septum cap under an argon balloon. An aliquot (1.5 mL, 10 μmol) of catalyst solution was then injected via gas-tight syringe. After stirring for 1 h at room temperature, the polymerization was quenched with ethyl vinyl ether (0.1 mL) and precipitated into vigorously stirred MeOH. The precipitate was collected by vacuum filtration using either a medium or fine porosity frit and dried under vacuum.

poly-5/
catalyst 2

Preparation of Poly-5 Using Catalyst 2.

Poly-5 was prepared according to the general procedure using catalyst **2**. NMR samples were prepared by stirring **poly-5** in $CDCl_3$. ^1H and ^{13}C NMR spectral assignments were consistent with literature reports.[5,6]

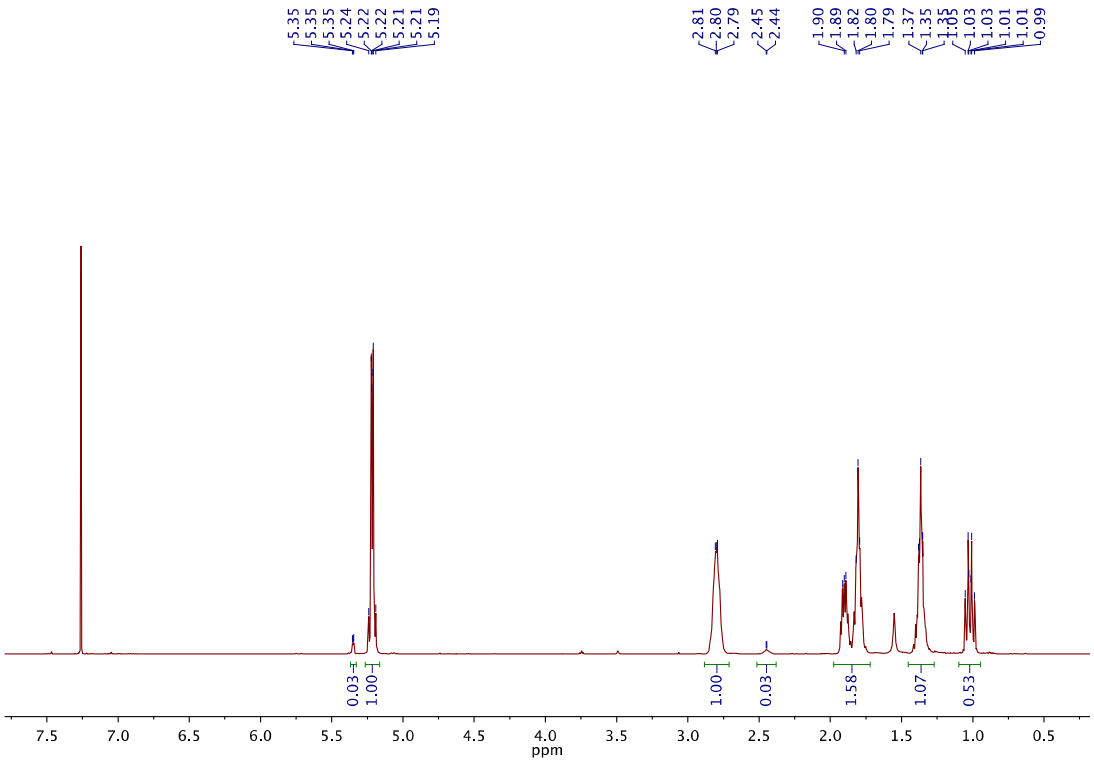


Figure S1. ^1H NMR (500 MHz, $CDCl_3$) spectrum of **poly-5** prepared with **2**.

[5] Al Samak, B.; Amir-Ebrahimi, V.; Corry, D. G.; Hamilton, J. G.; Rigby, S.; Rooney, J. J.; Thompson, J. M. *J. Mol. Catal. A: Chem.* **2000**, *160*, 13.
[6] Keitz, B. K.; Fedorov, A.; Grubbs, R. H. *J. Am. Chem. Soc.* **2012**, *134*, 2040.

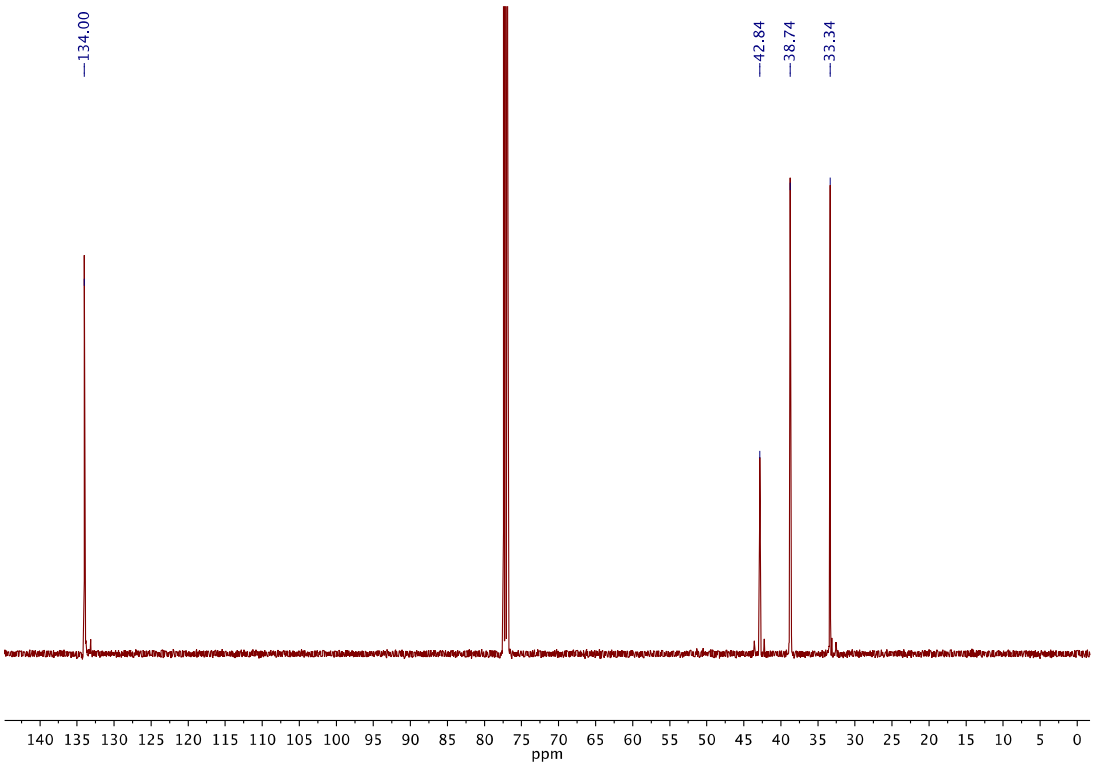


Figure S2. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **poly-5** prepared with **2**.

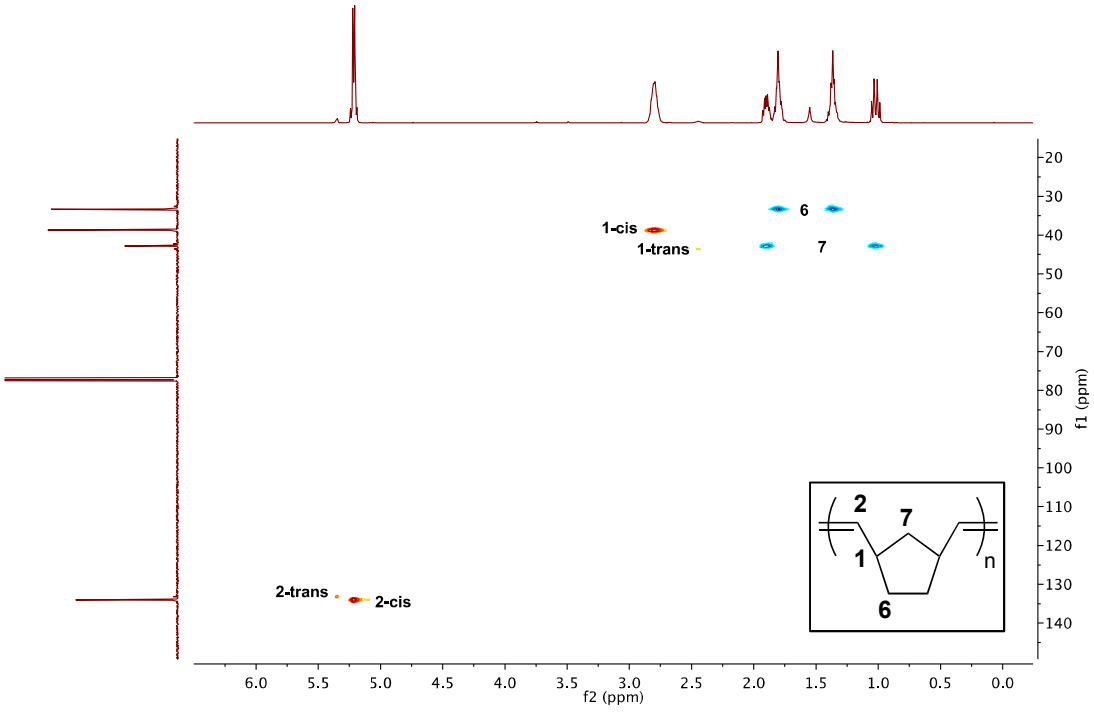


Figure S3. ^{1}H-^{13}C HSQC ($CDCl_3$) spectrum of **poly-5** prepared with **2**.

poly-5/ catalyst 3

Preparation of Poly-5 Using Catalyst 3.

Poly-5 was prepared according to the general procedure using catalyst **3**. NMR samples were prepared by stirring **poly-5** in $CDCl_3$. ^1H and ^{13}C NMR spectral assignments were consistent with literature reports.[5,6]

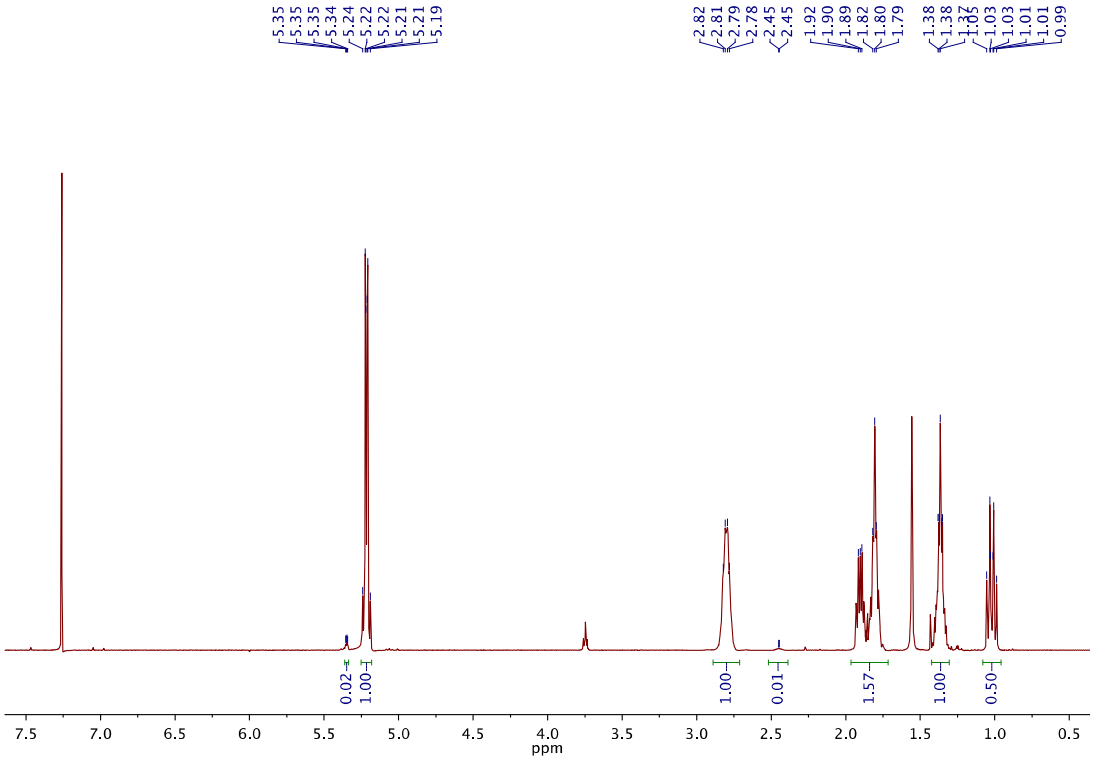


Figure S4. ^1H NMR (500 MHz, $CDCl_3$) spectrum of **poly-5** prepared with **3**.

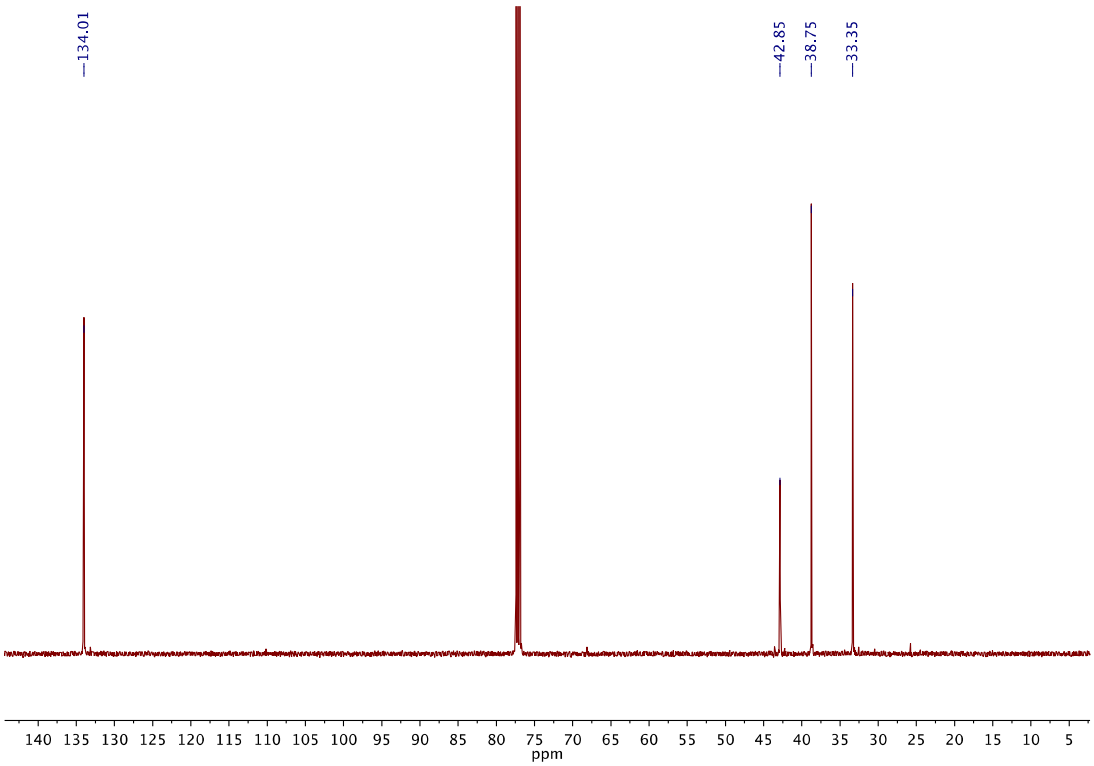


Figure S5. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **poly-5** prepared with **3**.

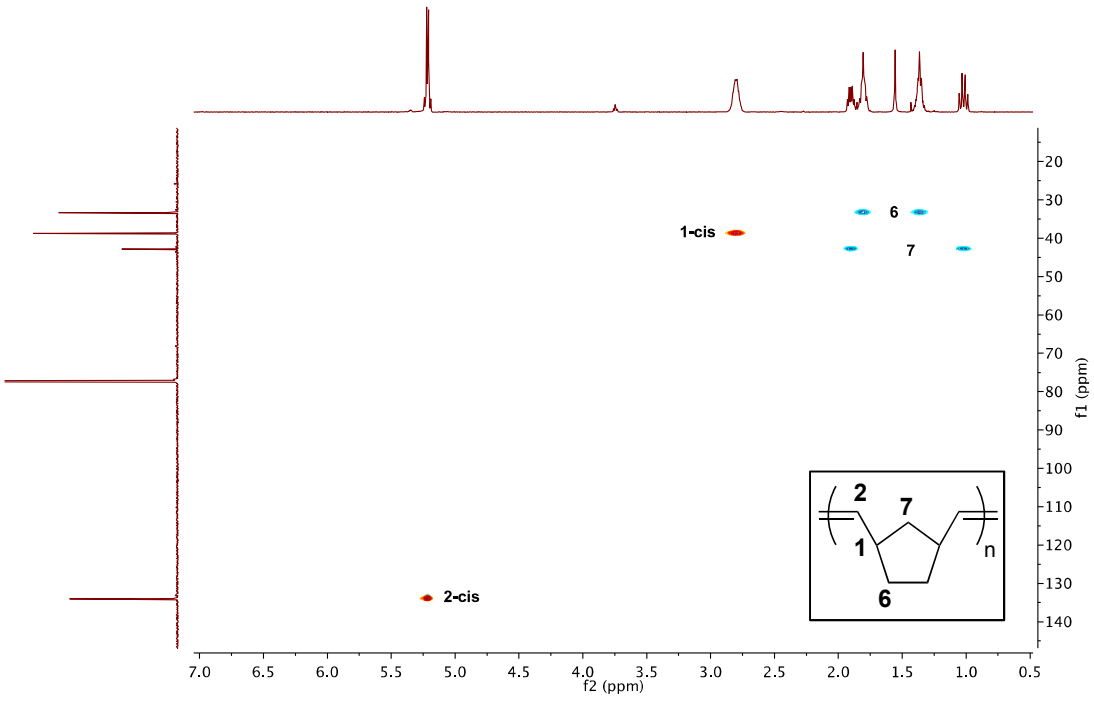


Figure S6. ^{1}H-^{13}C HSQC ($CDCl_3$) spectrum of **poly-5** prepared with **3**.

poly-5/ catalyst 4

Preparation of Poly-5 Using Catalyst 4.

Poly-5 was prepared according to the general procedure using catalyst **4**. NMR samples were prepared by stirring **poly-5** in $CDCl_3$. ^1H and ^{13}C NMR spectral assignments were consistent with literature reports.[5,6]

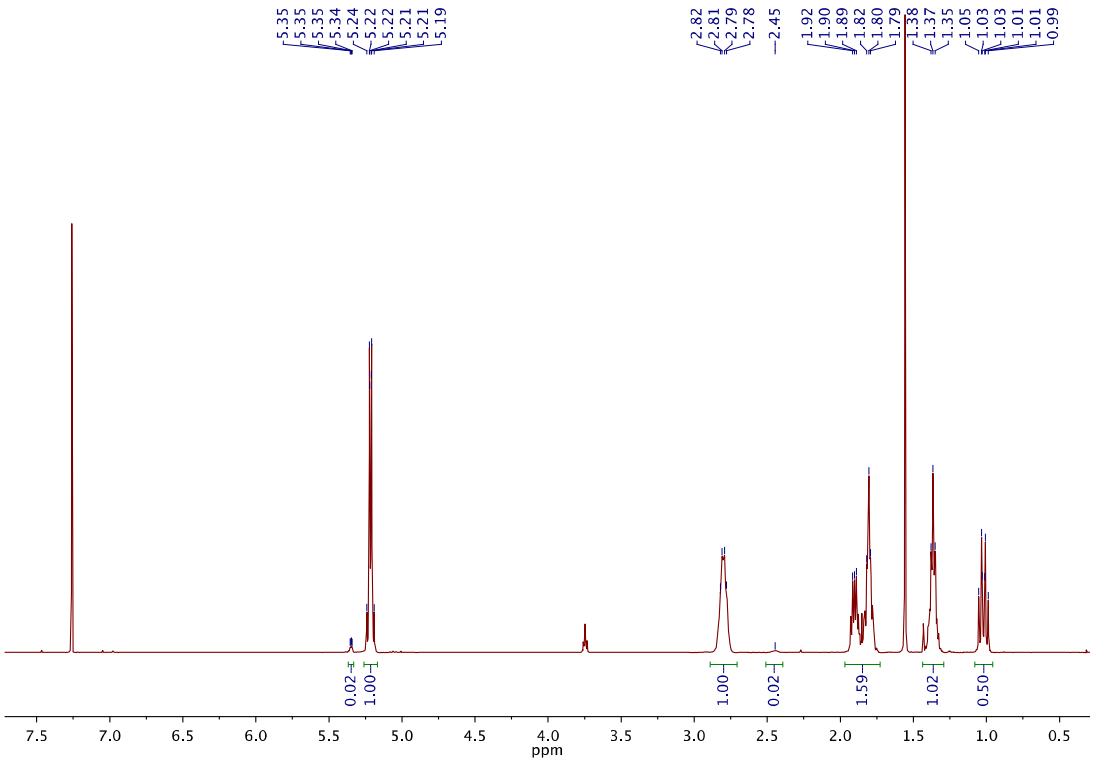


Figure S7. ^1H NMR (500 MHz, $CDCl_3$) spectrum of **poly-5** prepared with **4**.

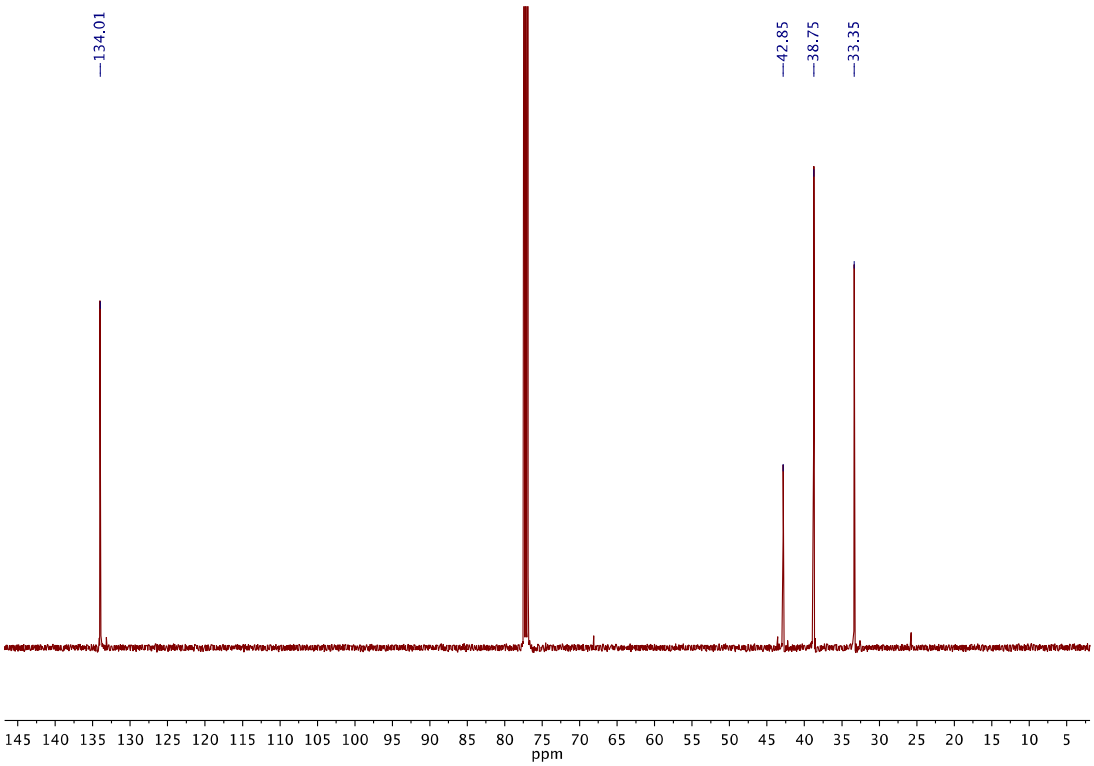


Figure S8. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **poly-5** prepared with **4**.

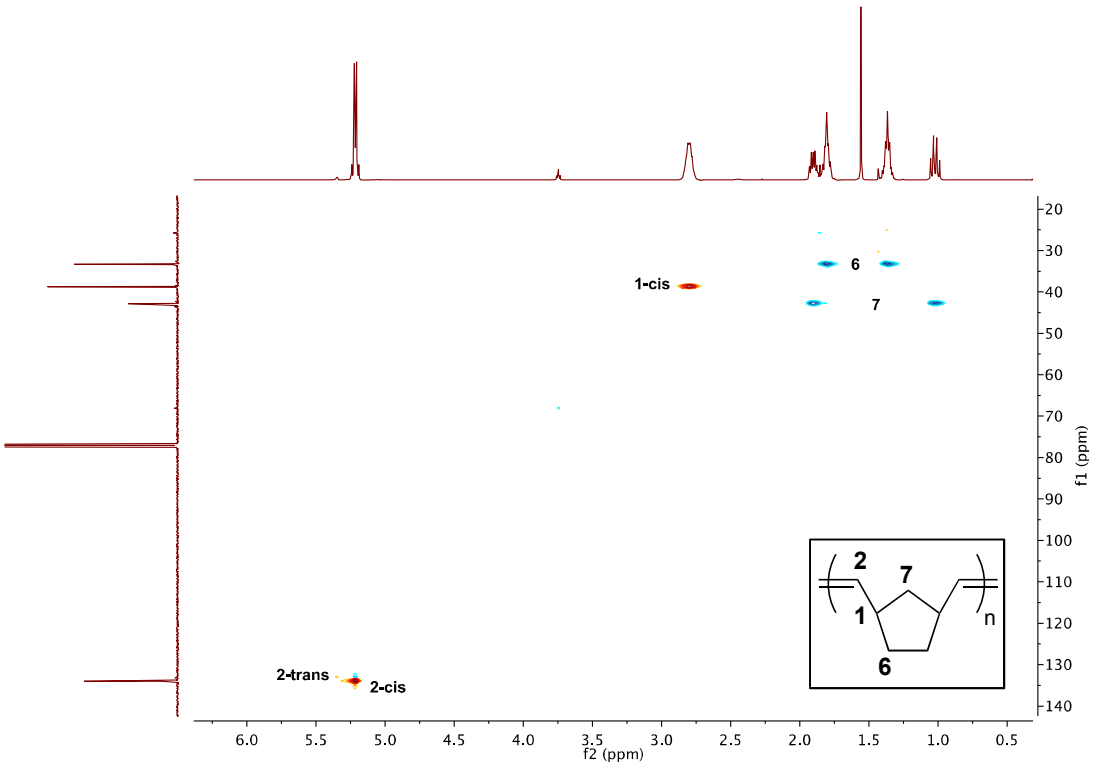
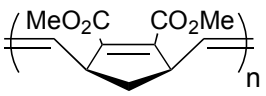


Figure S9. ^{1}H-^{13}C HSQC ($CDCl_3$) spectrum of **poly-5** prepared with **4**.



poly-6/ catalyst 2

Preparation of Poly-6 with Catalyst 2.

Poly-6 was prepared according to the general procedure using catalyst **2**. NMR samples were prepared by stirring **poly-6** in $CDCl_3$. Samples of **poly-6** prepared using catalysts **2**-**4** were virtually identical by ^1H and ^{13}C NMR. All ^1H and ^{13}C NMR spectral assignments were consistent with literature reports.[6,7]

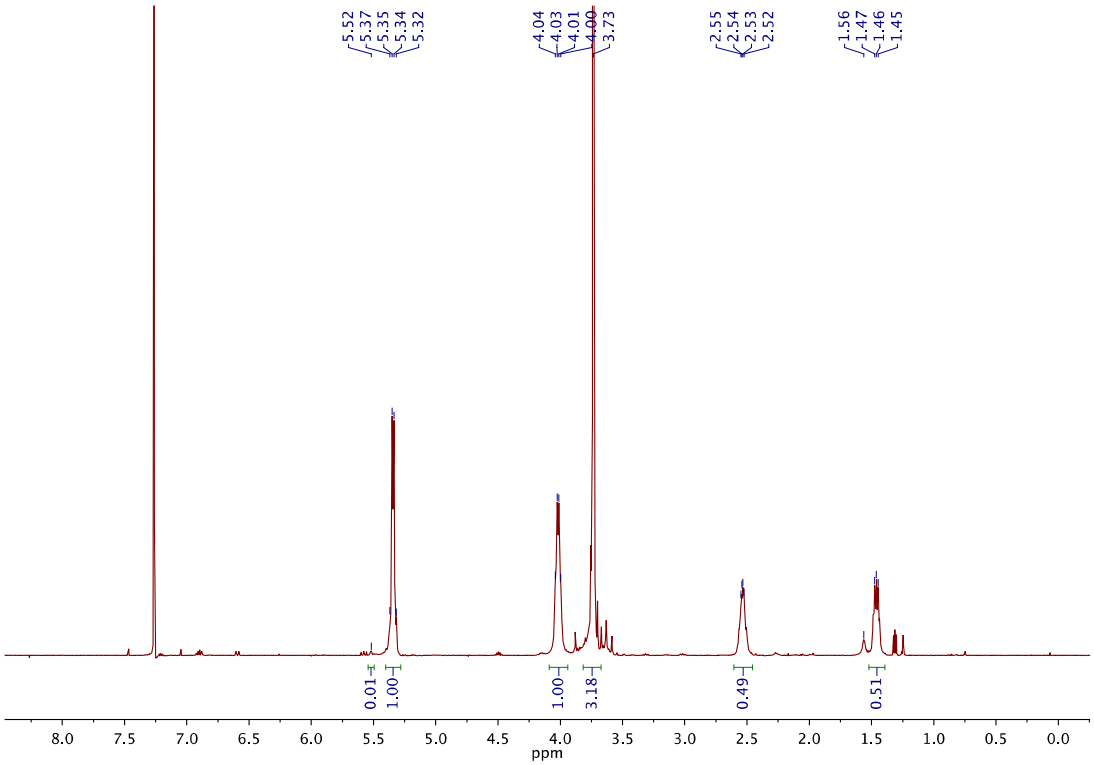


Figure S10. ^1H NMR (500 MHz, $CDCl_3$) spectrum of **poly-6** prepared with **2**.

[7] (a) McConville, D. H.; Wolf, J. R.; Schrock, R. R. *J. Am. Chem. Soc.* **1993**, *115*, 4413. (b) Flook, M. M.; Jiang, A. J.; Schrock, R. R.; Müller, P.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2009**, *131*, 7962.

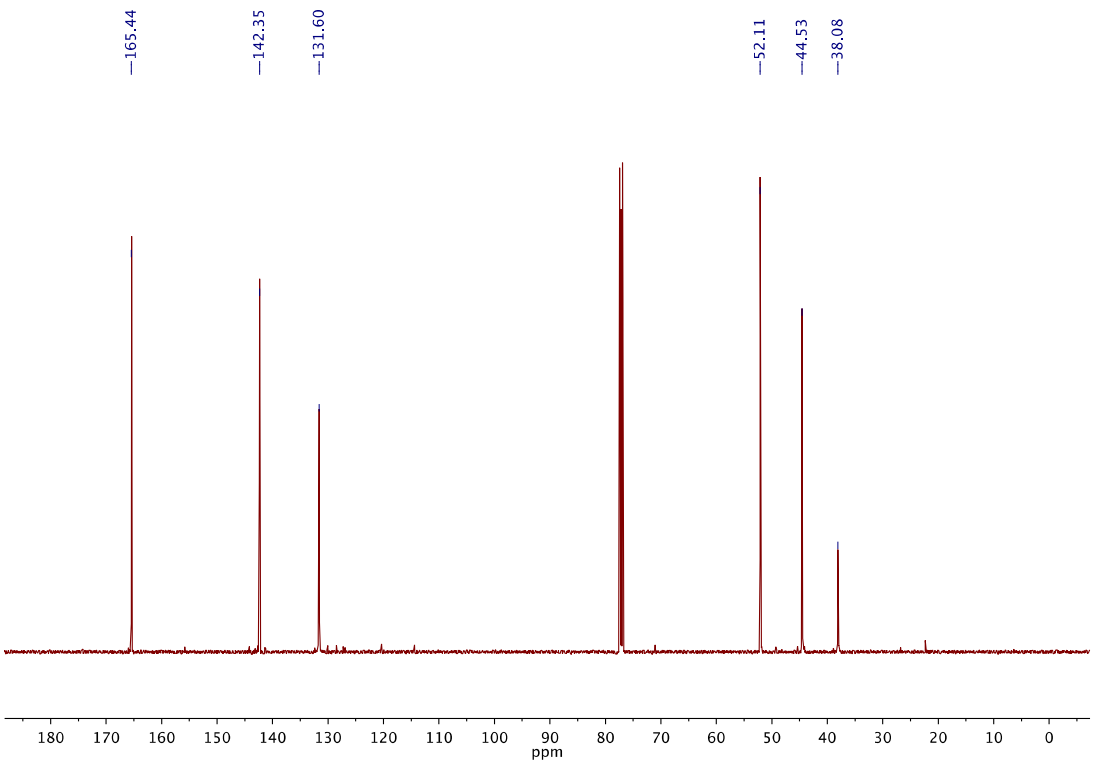


Figure S11. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **poly-6** prepared with **2**.

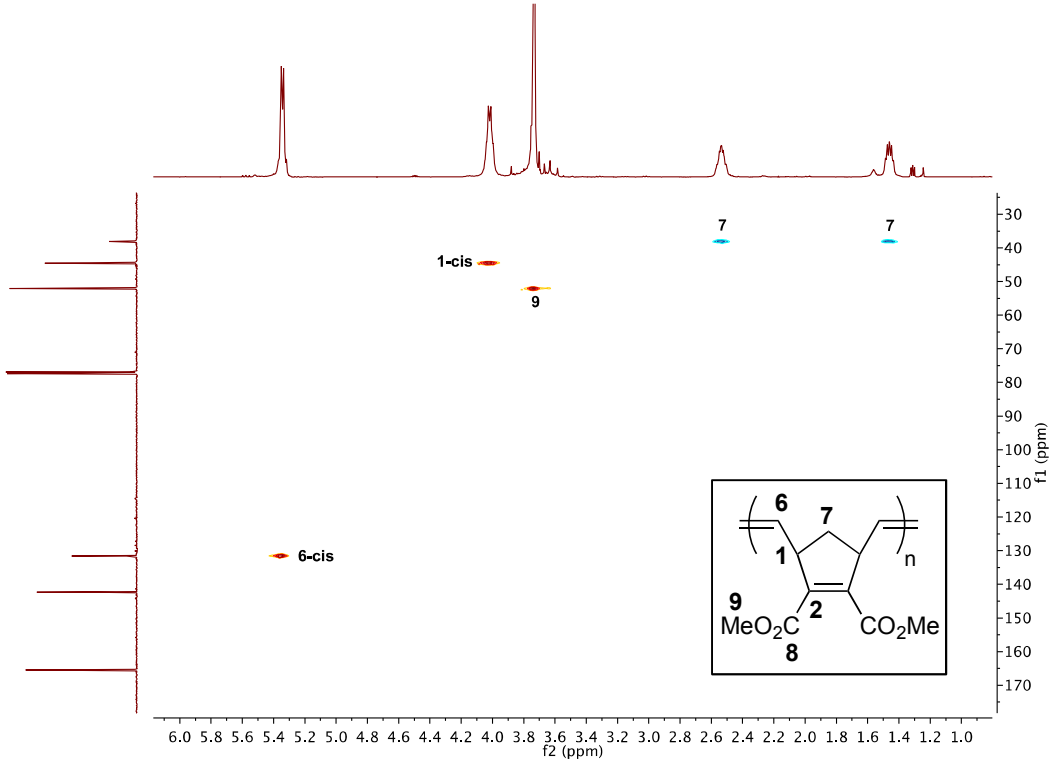
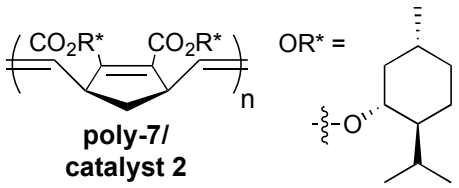


Figure S12. ^{1}H-^{13}C HSQC ($CDCl_3$) spectrum of **poly-6** prepared with **2**.



Preparation of Poly-7 Using Catalyst 2.

Poly-7 was prepared according to the general procedure using catalyst **2**. NMR samples were prepared by stirring **poly-7** in $CDCl_3$. ^1H NMR spectral assignments were consistent with literature data.[7b] ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.1 (CO), 164.1 (CO), 144.0 (C_2 or C_3), 140.1 (C_2 or C_3), 131.8 (C_5 or C_6), 131.6 (C_5 or C_6), 75.3 (CO_2CH), 75.0 (CO_2CH), 47.0, 46.9, 46.8, 45.0 (C_1 or C_4), 44.7 (C_1 or C_4), 41.1, 41.0, 38.5 (C_7), 34.5, 31.7, 25.7, 23.3, 22.3 (Me), 22.3 (Me), 21.2 (Me), 21.1 (Me), 16.5 (Me), 16.3 (Me).

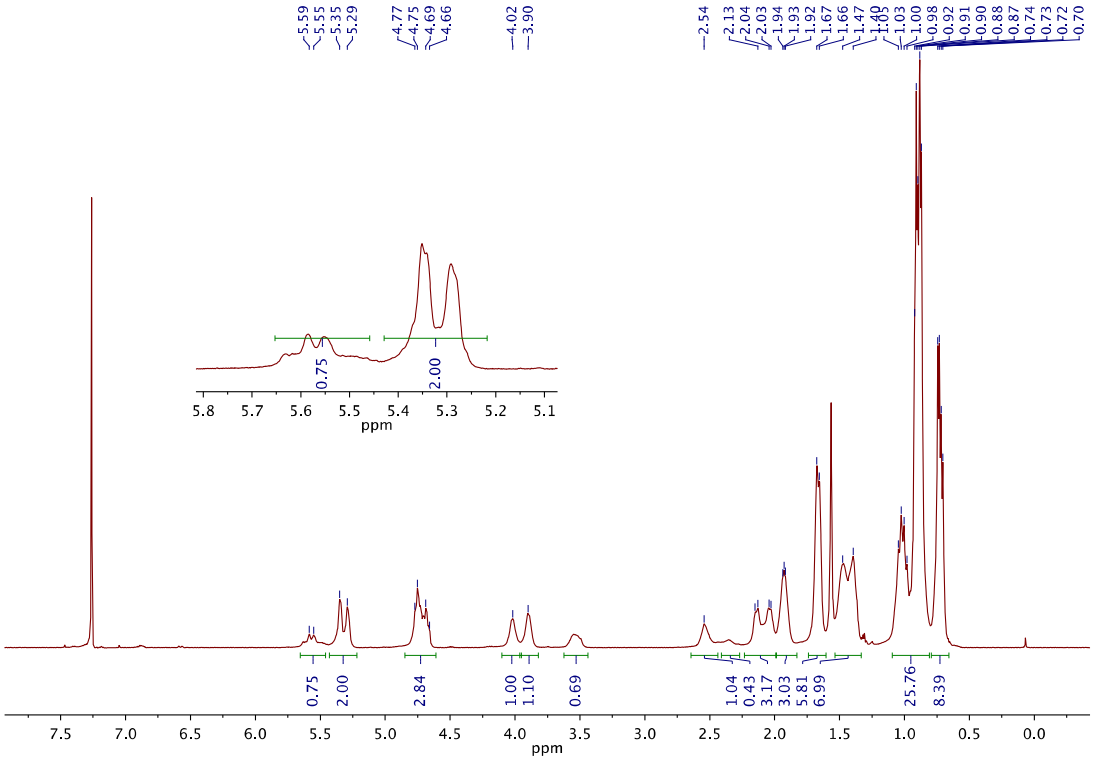


Figure S13. ^1H NMR (500 MHz, $CDCl_3$) spectrum of **poly-7** prepared with **2**.

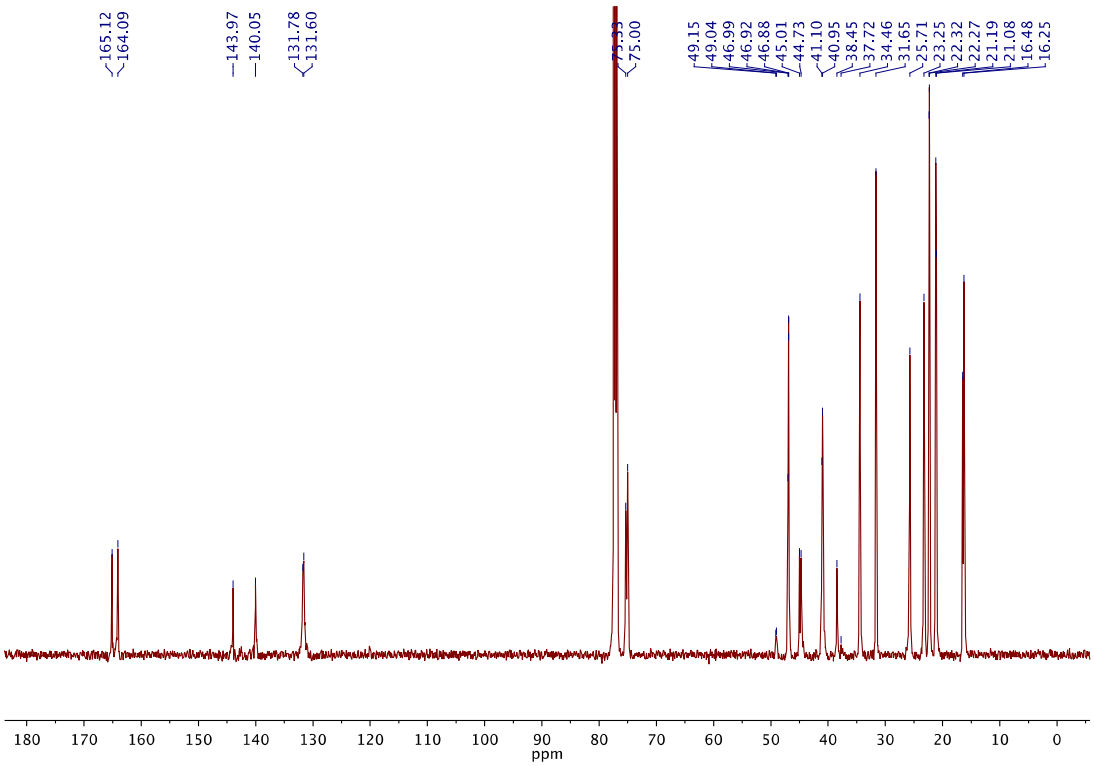


Figure S14. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **poly-7** prepared with **2**.

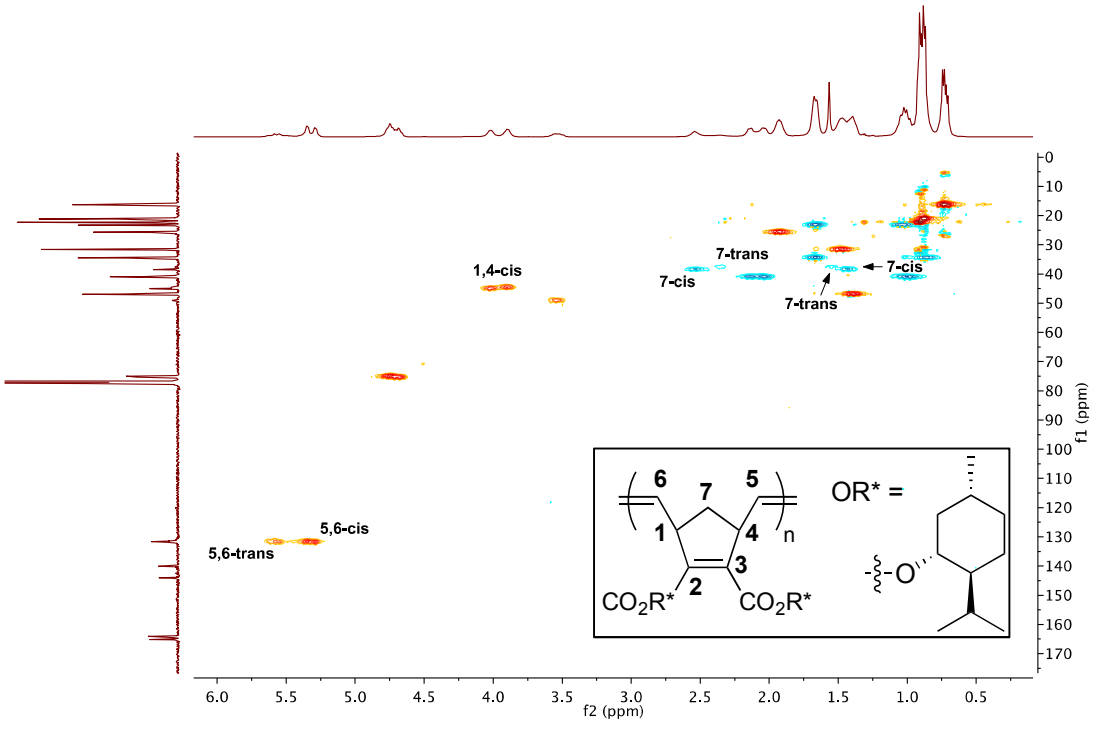


Figure S15. ^{1}H-^{13}C HSQC ($CDCl_3$) spectrum of **poly-7** prepared with **2**.

Samples of **poly-7** prepared using catalysts **2**-**4** were virtually identical by ^{1}H and ^{13}C NMR. The ^{1}H and ^{13}C chemical shifts of the minor compound were consistent with those reported for the trans, syndiotactic **poly-5**.[2a]

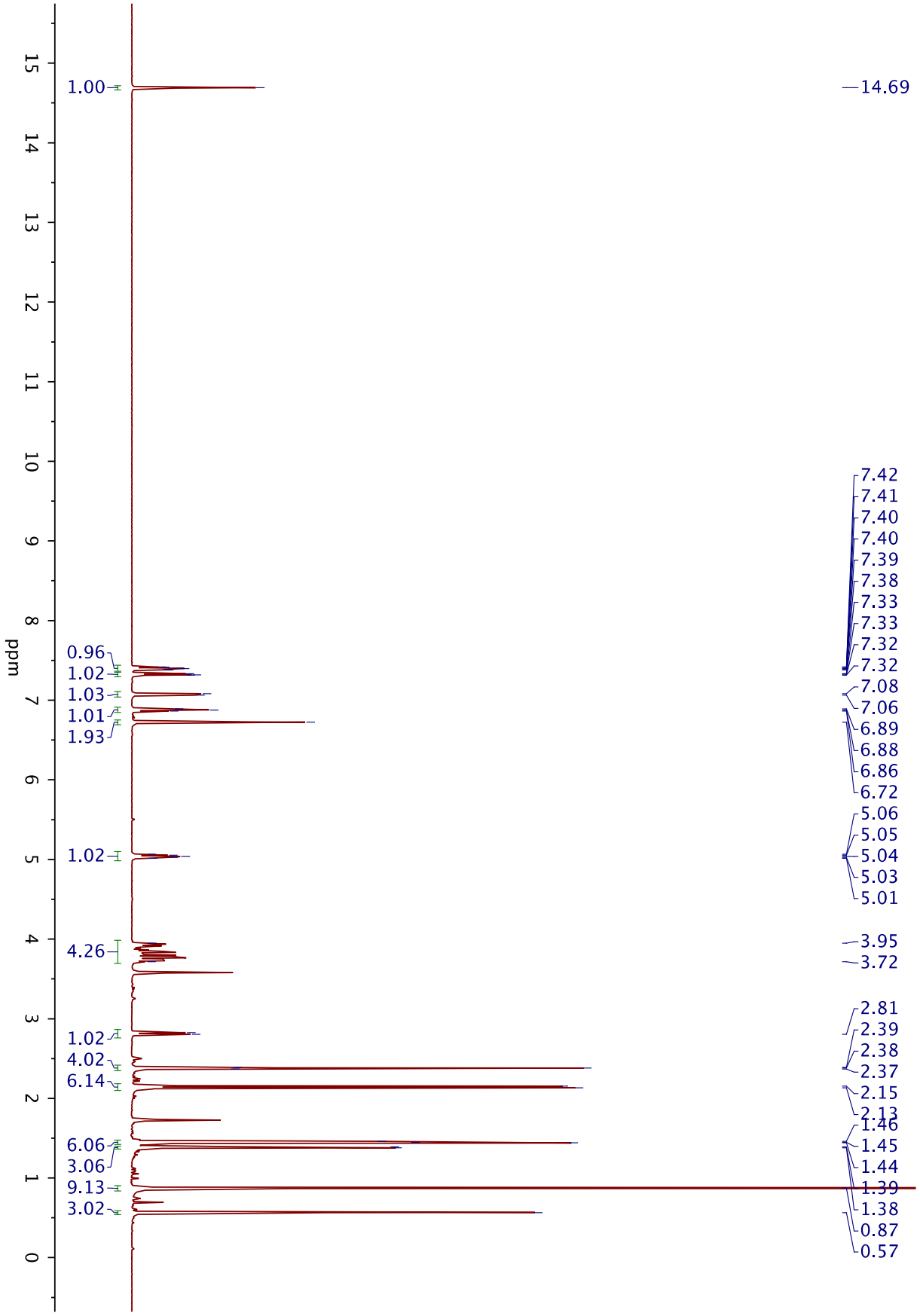


Figure S16. ^{1}H NMR (500 MHz, THF-d_8) spectrum of **2**.

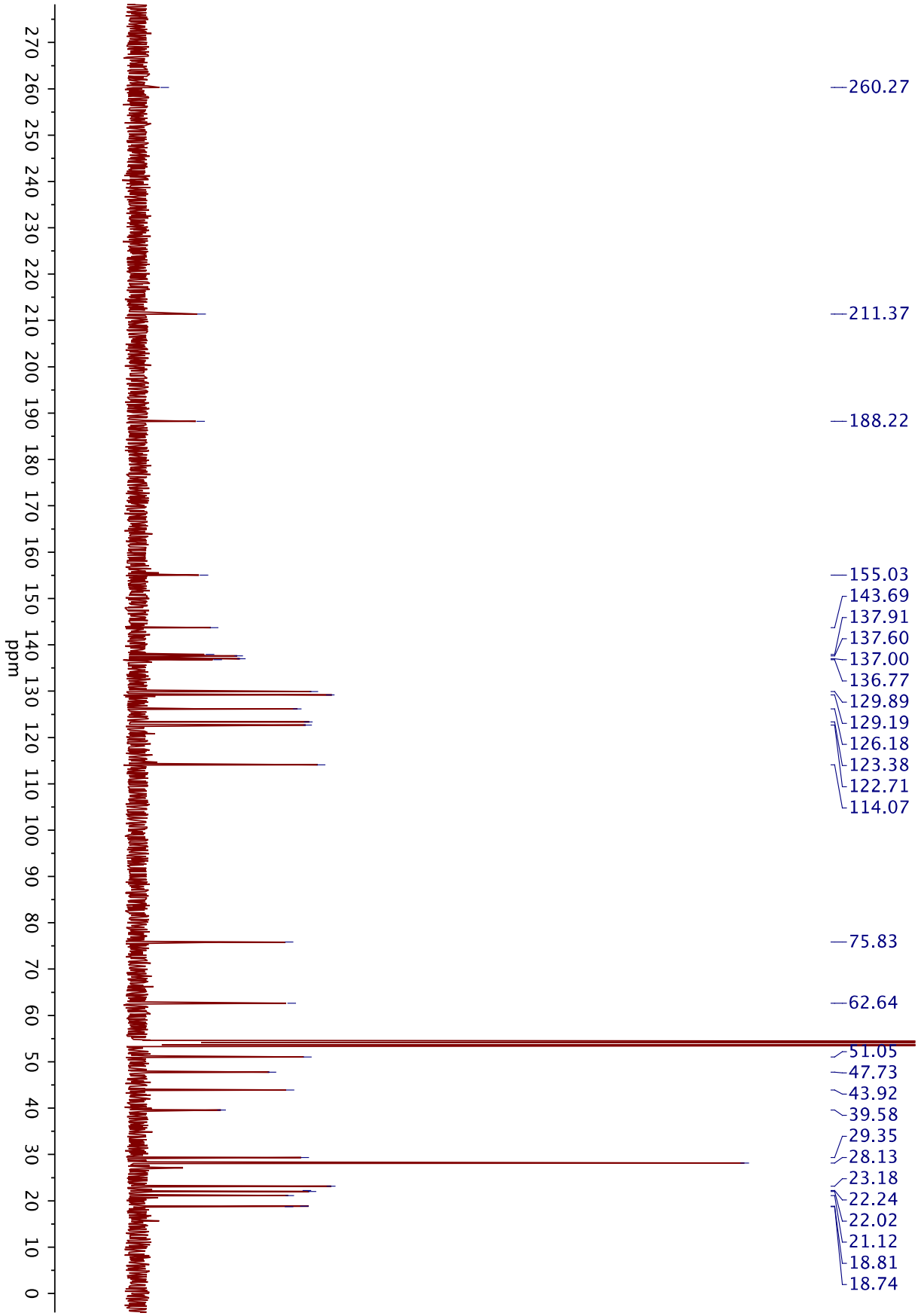


Figure S17. ^{13}C NMR (126 MHz, CD_2Cl_2) spectrum of **2**.

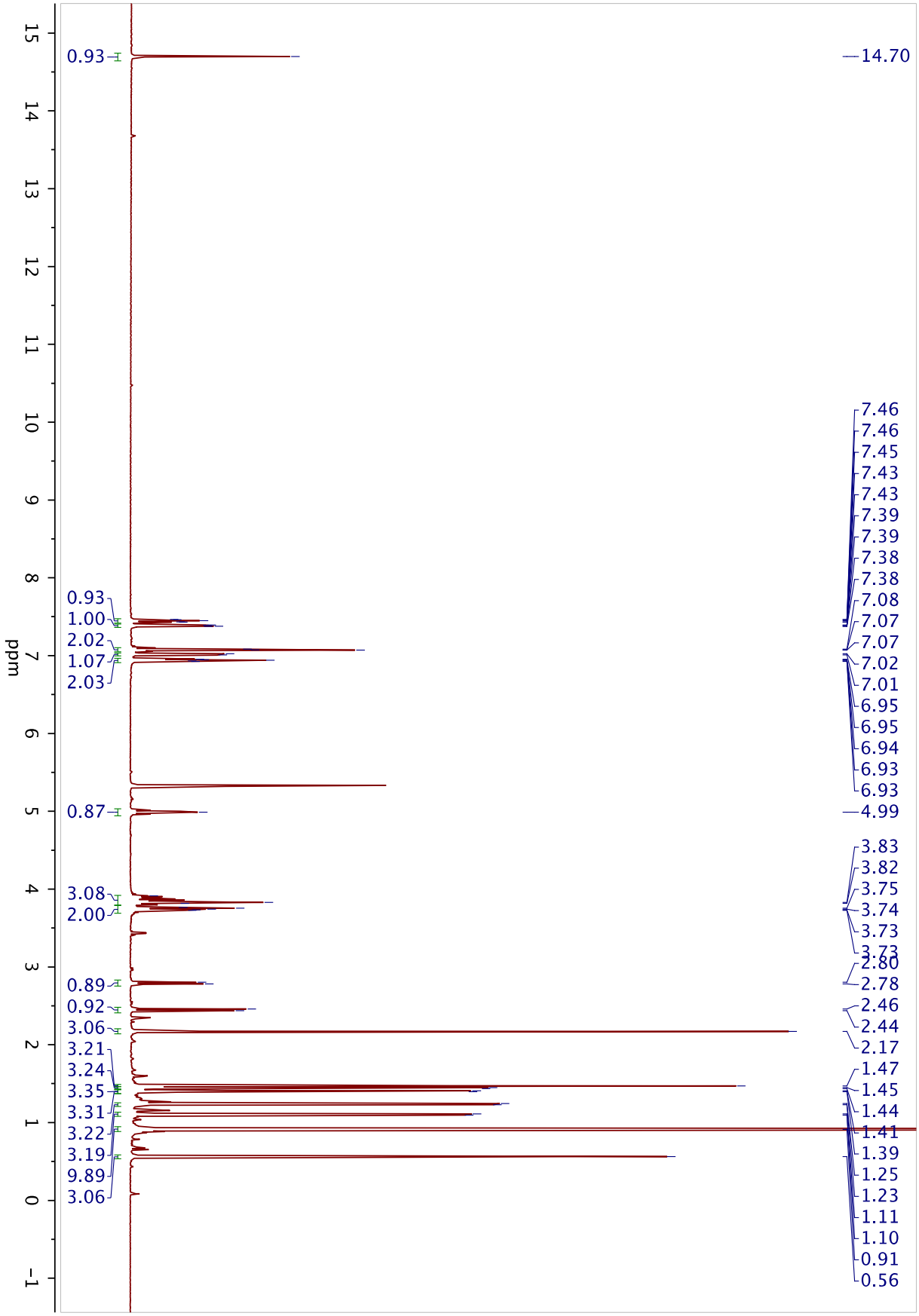


Figure S18. ^{1}H NMR (500 MHz, C_6D_6) spectrum of **3**.

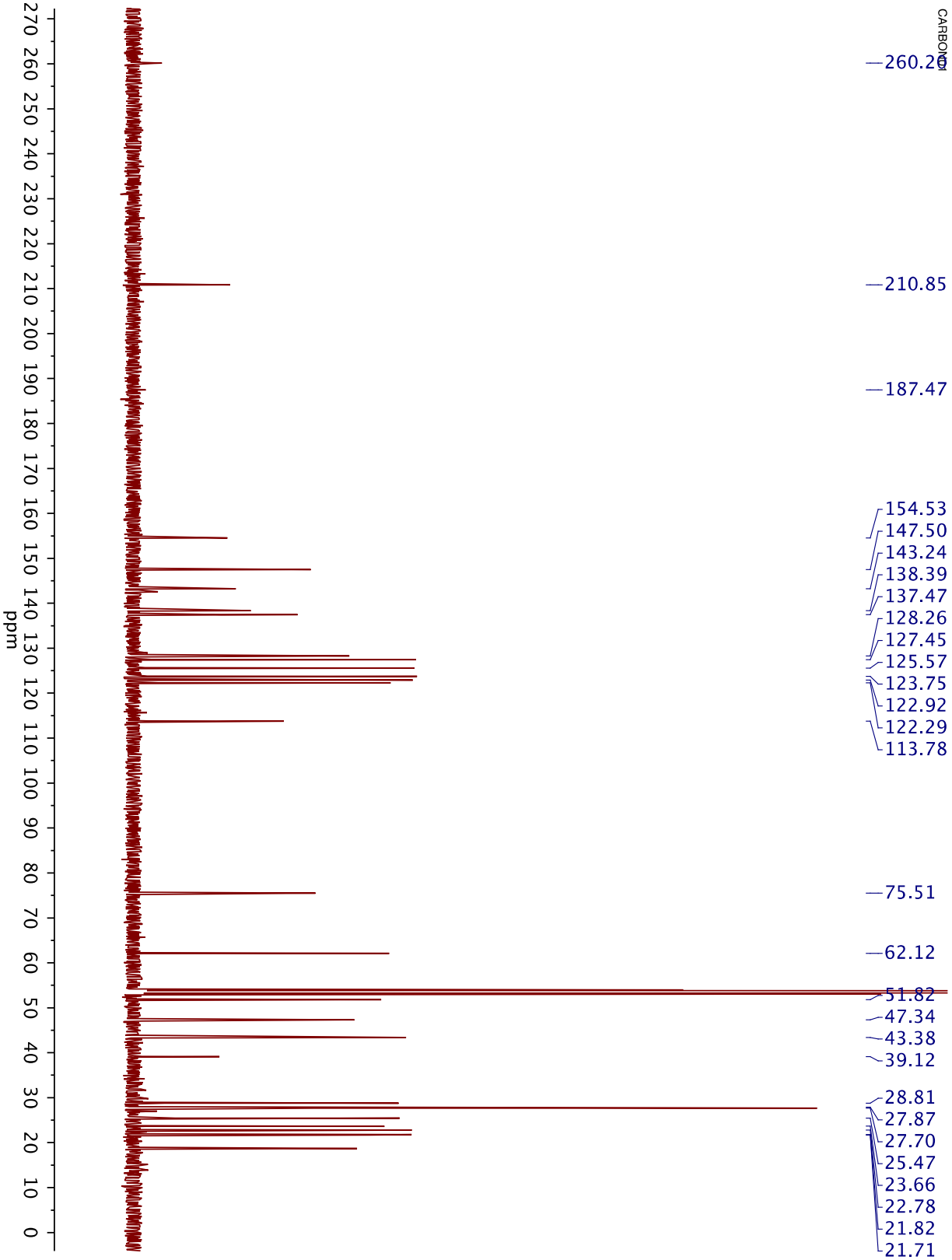


Figure S19. ^{13}C NMR (126 MHz, C_6D_6) spectrum of **3**.

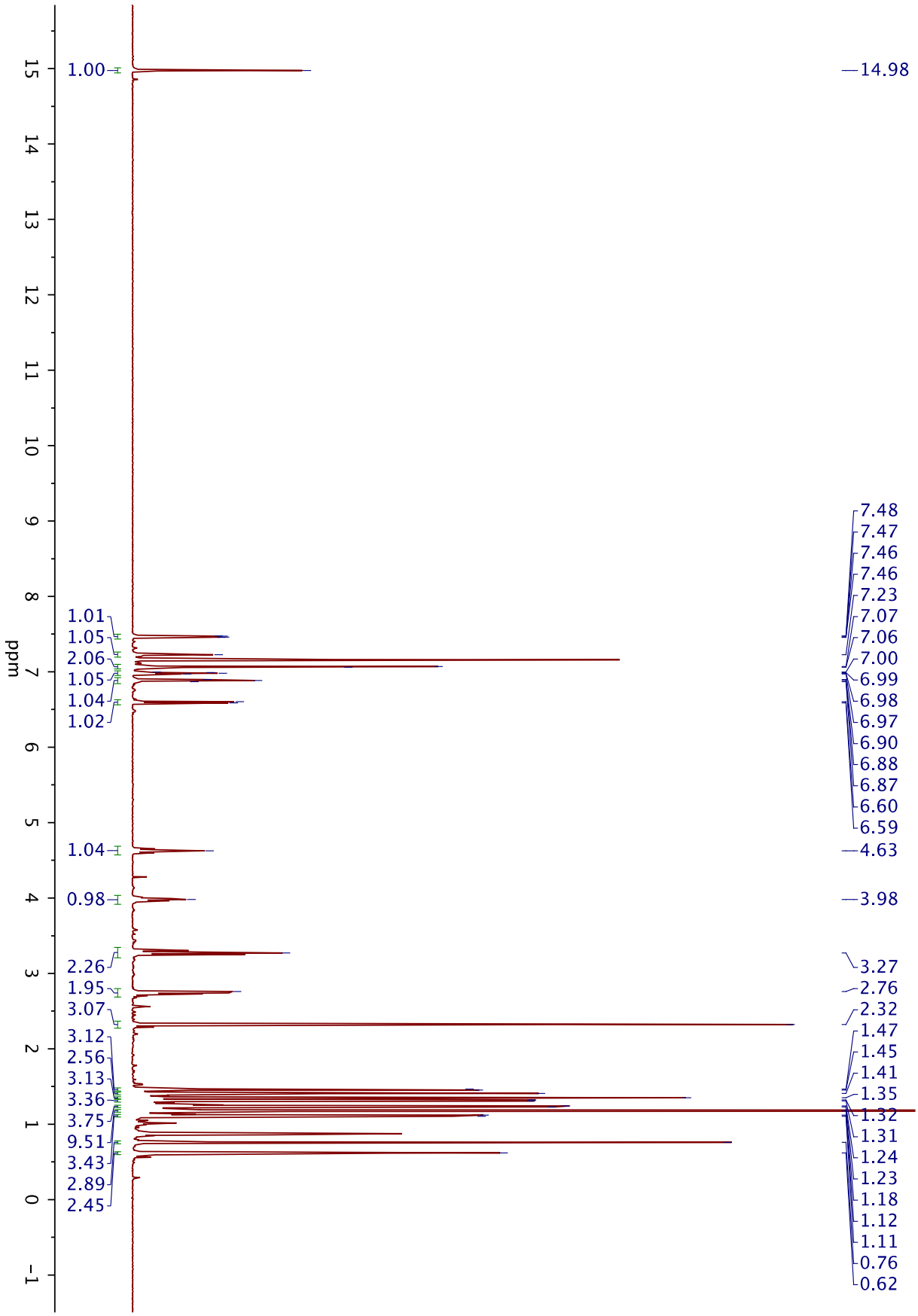


Figure S20. ^{1}H NMR (500 MHz, C_6D_6) spectrum of **4**.

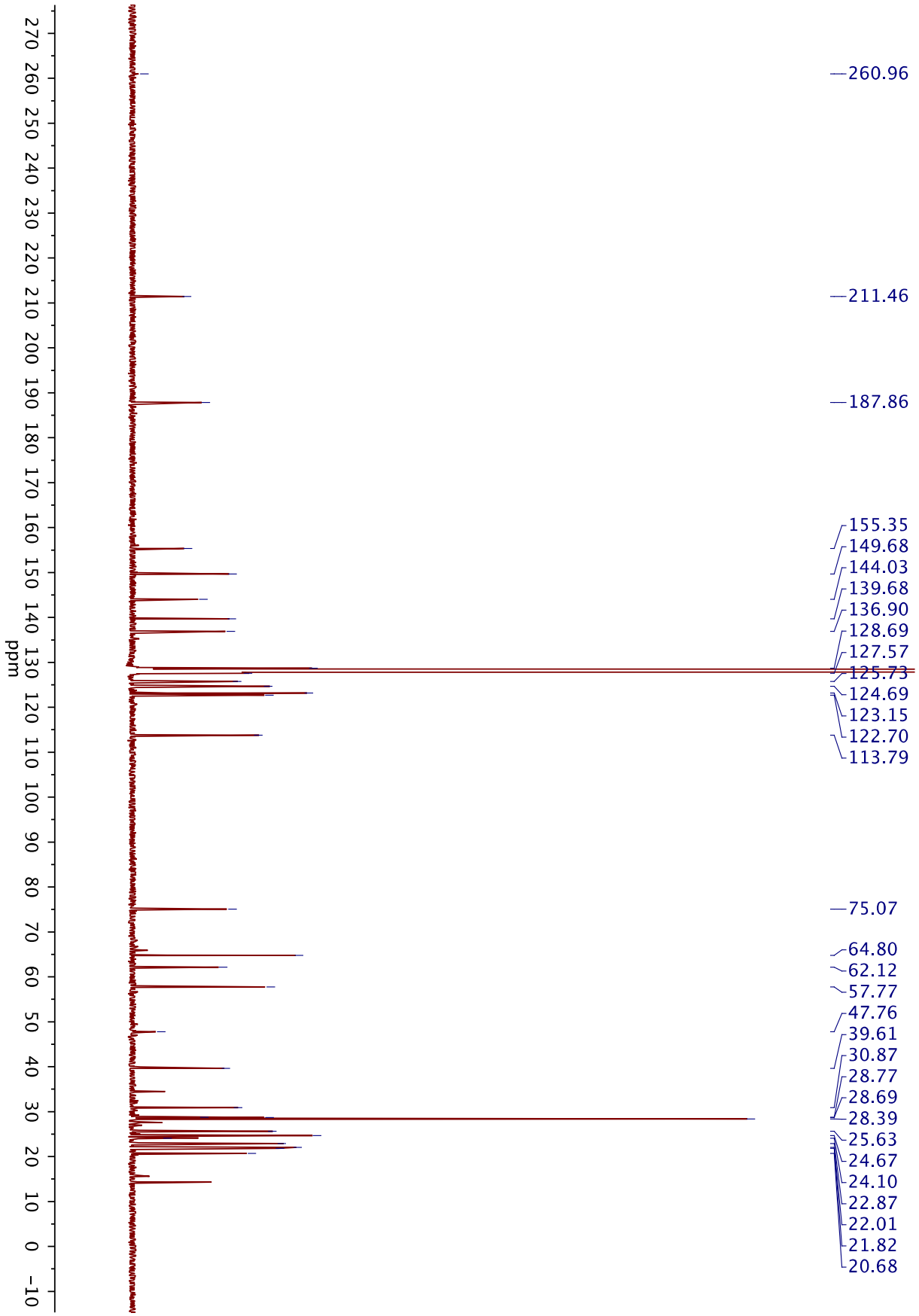


Figure S21. ^{13}C NMR (126 MHz, C_6D_6) spectrum of **4**.

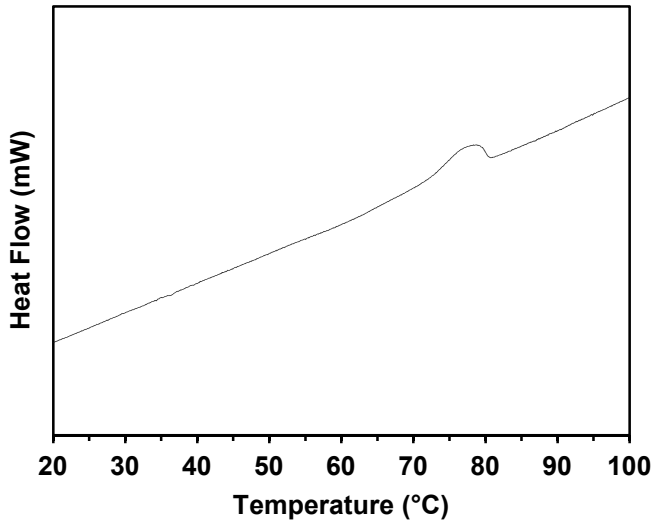


Figure S22. DSC curve for cis, syndiotactic **poly-5** prepared with catalyst **2**.

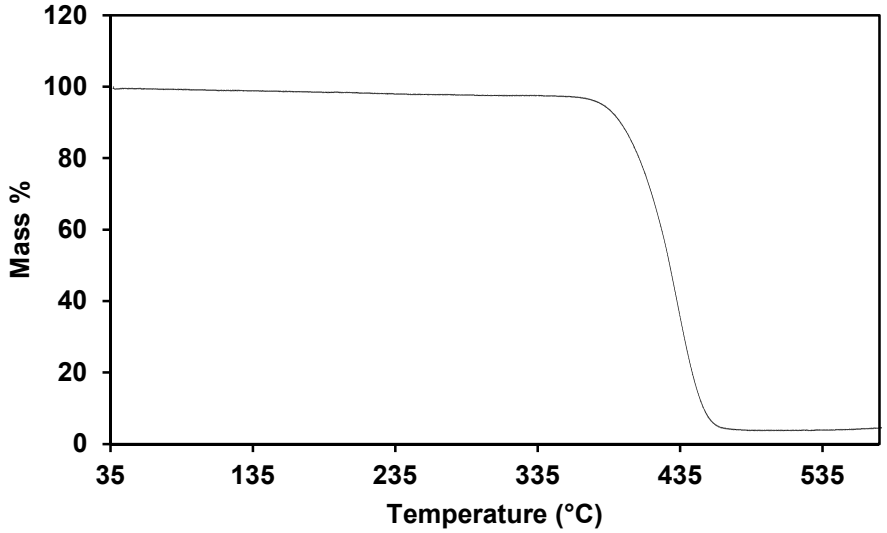


Figure S23. TGA curve for cis, syndiotactic **poly-5** prepared with catalyst **2**.

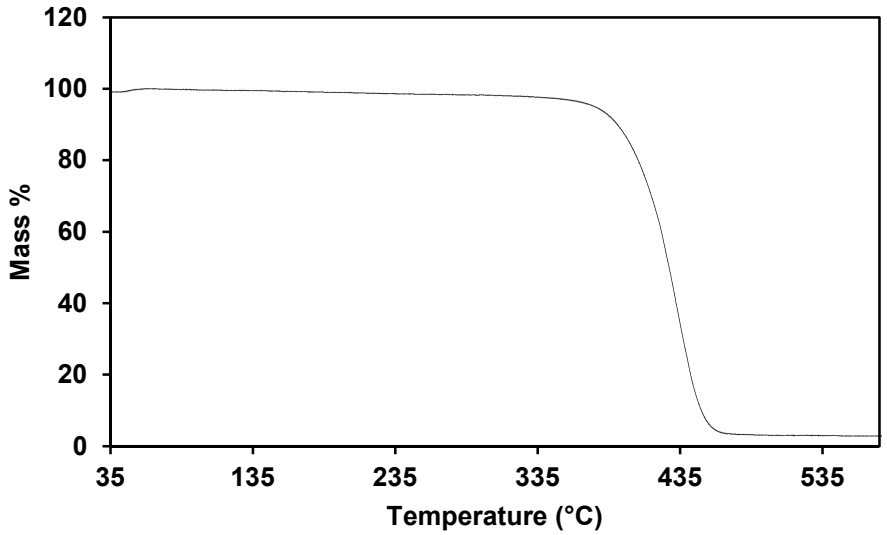


Figure S24. TGA curve for trans, atactic poly(norbornene) prepared with (1,3-Bis-(2,4,6-trimethylphenyl)-2-imidazolidinylidene)dichloro(*o*-isopropoxyphenylmethylene)ruthenium.